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14. ABSTRACT

To develop fundamental understanding on the material requirement of dielectric polymers in order to achieve high energy density with low loss and high dielectric strength. On the material front, the objective is to design and develop dielectric polymers of high energy density and low losses for pulse power applications. In the past three years, we have developed and investigated dielectric polymers with strongly coupled dipoles (modified PVDF based polymers) and their blends to achieve these objectives. Built upon the success of the polar-fluoropolymers, we have investigated a series of high temperature dielectrics with molecular units of high dipole moment and developed new class of polymer dielectrics based on aromatic polythiourea (ArPTU), which is capable of maintaining its low dielectric loss (high electric charge-discharge energy efficiency > 90%) up to an ultra high operation fields (> 1 GV/m) with a very high electric energy density (> 24 J/cm3). To develop understanding of the molecular and nano-structure mechanisms, a systematic dielectric studies, including the thermal stimulated discharge current (TSDC) measurement, have been carried out. Please see attached report for remaining abstract.

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Final Report

Ferroelectric Polymers with Ultrahigh Energy Density, Low Loss, and Broad Operation Temperature for Navy Pulse Power Capacitors

January 1, 2011 – December 31, 2013

ONR Grant No. N00014-11-1-0324

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Abstract:

The objective of this ONR program is to develop fundamental understanding on the material requirement of dielectric polymers in order to achieve high energy density with low loss and high dielectric strength. On the material front, the objective is to design and develop dielectric polymers of high energy density and low losses for pulse power applications. In the past three years, we have developed and investigated dielectric polymers with strongly coupled dipoles (modified PVDF based polymers) and their blends to achieve these objectives. Built upon the success of the polar-fluoropolymers, we have investigated a series of high temperature dielectrics with molecular units of high dipole moment and developed new class of polymer dielectrics based on aromatic polythiourea (ArPTU), which is capable of maintaining its low dielectric loss (high electric charge-discharge energy efficiency > 90%) up to an ultra high operation fields (> 1 GV/m) with a very high electric energy density (> 24 J/cm^3). To develop understanding of the molecular and nano-structure mechanisms, a systematic dielectric studies, including the thermal stimulated discharge current (TSDC) measurement, have been carried out. It was shown that it is the deep traps with high activation energy and large trap density in the PTU thin films that are responsible for the observed low conduction loss and high dielectric strength. Trap-limited high field conduction was studied by the electron hopping theory in the amorphous material.

By further tailoring the molecular structures, meta-aromatic polyurea which possesses a higher dipolar density than many polyureas reported in the literature has been synthesized. Preliminary experimental results show that an enhanced dielectric constant and higher energy density can be achieved in the new meta-aromatic polyurea.

Technical section:

Technical Objective: The objective of this program is to design and develop dielectric polymers of high energy density and low losses for pulse power applications. Systematically investigate several novel molecular and nano-structure approaches to realize dielectric polymers with high energy density and low losses, high temperature stability (> 150 °C) and high reliability of the dielectric polymers and capacitors made of these polymers.

Approaches:

1. Investigated crosslinking in the fluoropolymers to reduce the ferroelectric as well as conduction losses, using blends of P(VDF-HFP) and P(VDF-CTFE) with low loss polymers (with higher temperature stability) to reduce the ferroelectric losses and improving the high temperature stability.[1-3]
2. Developed new class of aromatic polythiourea dielectrics, which has a high energy density, high dielectric strength and low loss, based on high dipole moment with weak coupling dipoles. Investigate the synthesis, effects of defects, and structures in the thin films to understand the breakdown mechanisms and high field properties. [4-7]

3. Investigated the conduction mechanism and defects structures to understand the breakdown mechanisms and high field properties for the aromatic polythiourea dielectrics, which exhibits a high energy density, high dielectric strength and low loss.
4. Further studied the effect of molecular structures on the dielectric response and developed a new meta-aromatic polyurea which exhibits a dielectric constant near 6, much higher than that of BOPP with low loss at high electric field (> 600 MV/m).[8]

Progress Statement Summary:

We have investigated a polymer blend approach to improve the dielectric losses of P(VDF-CTFE) while maintaining a high energy density.

We have developed new class of aromatic polythiourea dielectrics, which has a high energy density, high dielectric strength and low loss, and systematically studied the defects structures responsible for the low dielectric loss and high dielectric strength in the aromatic polythiourea films. It was found that the trap-limited high field conduction can be described well by the electron hopping theory. The high field conduction mechanism features a small conduction current (~10^{-7} A/cm^2) and very slowly increasing current density (α ~ 6 cm/V). The thermally stimulated discharge current study revealed the presence of deep level traps, which are caused by the high dipole moment, with high activation energy(> 2eV) and large trap density(10^{15}) in the PTU thin films.

We have worked on tailoring the molecular structures of polyureas and polythioureas to study the molecular and nanostructures that can lead to even higher energy density and lower loss with high thermal stability. Meta-polyurea with higher dielectric constant by increasing the volumetric dipole density was synthesized, leading to a dielectric film with a dielectric constant near 6.

Progress:

1. Crosslinked polar-fluoropolymer blends

We investigated a polymer blend approach to improve the dielectric losses of P(VDF-CTFE) while maintaining a high energy density. In this approach, in order to effectively reduce the dielectric losses, especially the losses at high fields, it is necessary that the low loss polymer in the blends mixes well with P(VDF-CTFE) to eliminate macro-phase separation, thus effectively interrupting long range polar-correlation and conduction, both of which lead to high losses, induced at high electric fields. In this study, we demonstrate that poly(ethylene-chlorotrifluoroethylene) (ECTFE) which has a dielectric constant of 2.6 and a very low loss of 0.18% can form high quality transparent blend films with P(VDF-CTFE), thus producing blend films with a much reduced loss (~1%) while maintaining relatively high dielectric constant (K~7), compared with the neat P(VDF-CTFE) copolymer. Moreover, crosslinking the blend in the melt can further improve the mixing of two polymers at the nanoscale, thus leading to a dramatic reduction of high field losses in the blend. In turn, reduced losses also result in an increase in the discharged energy density, compared with the blend without crosslinking. ECTFE also possesses other features: (i) the common CTFE and VDF monomers in both P(VDF-CTFE) and ECTFE makes it easier to form blends and the common CTFE monomer is desired for the crosslinking, (ii) The melting temperature T_m (~242 °C) is within the temperature range to optimize the melt process (extrusion) of the blend films.

Presented in Figure 1 is a comparison of the P-E loops of pure P(VDF-CTFE) films with those of the blend and crosslinked blend films. At low fields (<10 MV/m), P(VDF-CTFE) 91/9 mol% copolymer exhibits a room temperature dielectric constant of 12 and a loss of 3.5% with a non-polar crystal structure.[9] However, the isolated random defects due to CTFE seem not strong enough to prevent the formation of large polarization domains under high applied electric

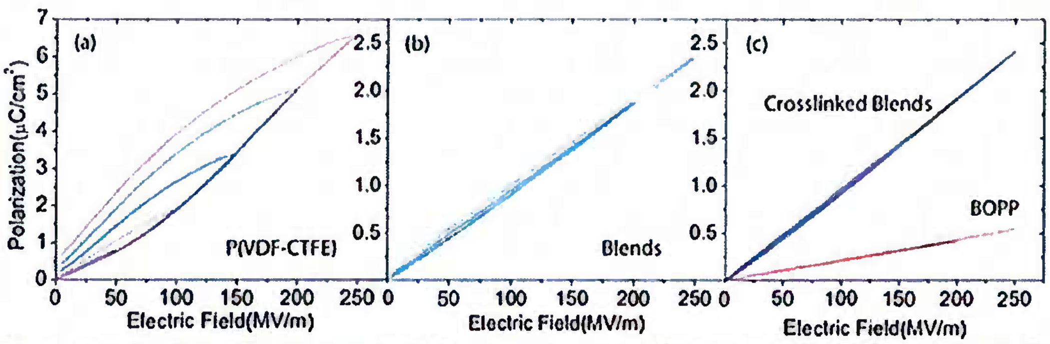


FIG. 1. Polarization -Electric Field (D-E) response of (a) P(VDF-CTFE) 91/9 mol%, (b) P(VDF-CTFE)/ECTFE 67/33 wt% blends, (c) P(VDF-CTFE)/ECTFE 67/33wt% blends with crosslinking under uni-electric fields (different curves correspond to driving fields of different amplitude). For the comparison, the D-E response of a commercial biaxially oriented polypropylene film is also presented in (c).

fields and consequently, the copolymer exhibits a non-linear increase of losses at high field from the polarization hysteresis as revealed by the large polarization hysteresis at fields > 100 MV/m. Besides, P(VDF-CTFE) copolymer also suffers a high conduction loss at high fields.[10,11] In contrast, both the blend and crosslinked blend films exhibit a much reduced losses at high field (Figures 1(b) and 1(c)). More interestingly, the crosslinking can cut down the high field loss without reducing the energy density as shown in figure 2.

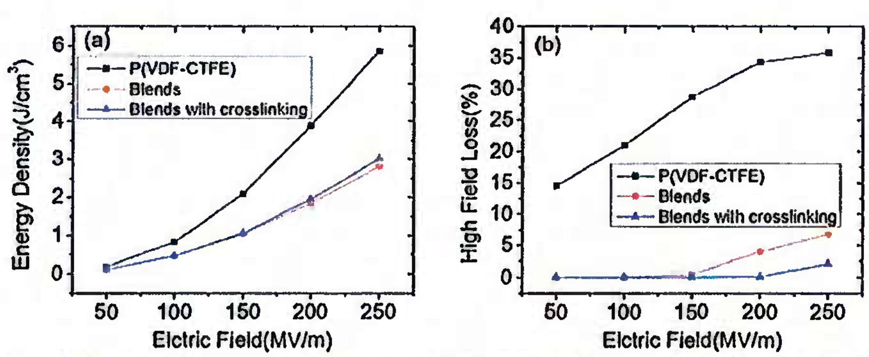


FIG. 2. (a) Discharged energy densities and (b) high field losses of pure P(VDF-CTFE) and blends films as a function of applied field amplitude.

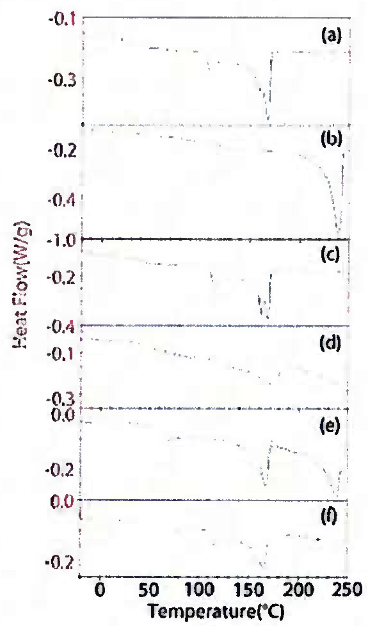


FIG. 3. DSC data of (a) P(VDF-CTFE), (b) ECTFE; (c) crosslinked P(VDF-CTFE), (d) crosslinked ECTFE; (e) P(VDF-CTFE)/ECTFE 67/33 wt% blends, (f) Crosslinked P(VDF-CTFE)/ECTFE 67/33 wt% blends

To provide some understanding on the difference between the blend film and the crosslinked blend film, we carried out a DSC study of the two blend films (Figures 3(e) and (f)). For the comparison, DSCs of pure and corsslinked P(VDF-CTFE) (Figures 3(a) and (c)) and pure and crosslinked ECTFE (Figures 3(b) and (d)) were also measured. The high transparency of the blend films indicates that the two polymers in the blend do not have macrophase separation. The DSC data in Figure 3 show that the blend film displays two melting peaks, one for ECTFE (T_m~240 °C) and the other for P(VDF-CTFE) (~160 °C), which are the same as the melting temperatures of the two pure polymers. This suggests that P(VDF-CTFE) and ECTFE are partially miscible in the melt and crystallization of each component results in separated P(VDF-CTFE) and ECTFE crystals, which in turn reduces the cooperativeness among P(VDF-CTFE) polarization domains and consequently hysteresis loss. [12]

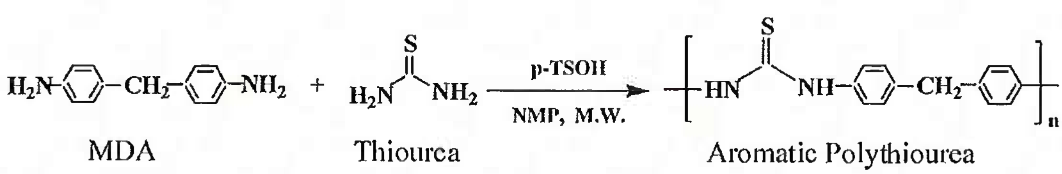
Comparison of figures 3(a) and 3(c) reveals that crosslinks do not induce marked changes in the melting features of P(VDF-CTFE). In contrast, it causes a large change of melting in ECTFE (figures 3(b) and 3(d)), which is likely caused by the fact that the crosslinks occur in the CTFE units in the copolymer and P(VDF-CTFE) 91/9 mol% copolymer has much lower CTFE content compared with ECTFE, which has 50 mol% of CTFE in the copolymer. For the crosslinked blends, DSC shows an melting peak ~ 180 °C which is probably from the crosslinked ECTFE and is higher than that in figure 3(d) (T_m~170 °C), suggesting that the crystalline phase of ECTFE is affected by the inter-molecular interactions with P(VDF-CTFE) due to better miscibility in the molten state and even smaller size phase separation (and crystallite sizes). Earlier experiment results have demonstrated that crosslinking in P(VDF-CTFE) will reduce the losses at high fields.[10] It is because compared with the isolated CTFEs which act as random defects to break up the large polarization domains in PVDF, crosslinks have much stronger effect against the formation of large polarization domains induced by high applied electric fields. Formation of large polarization domains under high fields causes large ferroelectric hysteresis loss. In the crosslinked blends, the higher CTFE contents result in an increased crosslinking density, which can lead to lowered losses at high fields. Therefore, the improved nanoscale mixing of the two polymers and increased crosslinking density further cut down the losses from the ferroelectric switch and conduction process, yielding a dielectric film with a high energy density and low losses at high electric fields in the crosslinked blend films.

2. Aromatic polythiourea dielectrics with ultrahigh breakdown strength, low dielectric loss, and high electric energy density

We have developed a new class of dielectric polymer based on aromatic polythiourea (ArPTU), which is a polar polymer capable of maintaining its low dielectric loss up to very high operation fields (> 1 GV/m) with a very high electric energy density (> 20 J/cm^3). The thiourea unit has a high dipole moment (~ 4.89 D), leading to a dielectric constant of 4.5, which is more than twice of that of BOPP and higher than most linear dielectric polymers. [13,14] Moreover, different from the strongly coupled dipolar polymers such as PVDF, which are semicrystalline, ArPTU is an amorphous, glass-phase polymer, with weak coupling among the dipoles. Consequently, there is no polarization hysteresis loss even at the highest measured electric field (1.1 GV/m). It should also be noted that even with the strong dipolar moment of thiourea units, the polymer is not sensitive to moisture, which is very attractive for practical dielectric applications.[15] This unusual property of polythiourea is likely due to the hydrophobic aromatic rings immediately surrounding the thiourea unit in the polymer chains.

2.1. Synthesis, results and discussions

ArPTU was synthesized via microwave-assisted polycondensation of 4,4'-diphenylmethanediamine (MDA) with thiourea in N-methyl-2-pyrrolidone (NMP) with p-toluenesulfonic acid (p-TSOH) as a catalyst (Scheme 1). The solution was irradiated in a microwave at 200-Watts power for 7 minutes, followed by a second irradiation of 400 watts for 8 minutes. After purification, polythiourea was isolated as a powder, and polymer films with thicknesses ranging from 1 μm to 5 μm were prepared by spin casting on 1 cm x 1 cm silicon substrates coated with aluminum electrodes. The films were dried in a vacuum at 25 °C for 3-4 hours, then at 110 °C overnight, followed by an annealing process at 140 °C for 12 hours.



Scheme 1. Schematic of synthesis of polythiourea via microwave-assisted polycondensation of 4,4'-diphenylmethanediamine (MDA) and thiourea.

Figure 4 presents the dielectric constant and loss tangent over broad temperature from -25 °C to 150 °C and 100 to 1M frequency. Basically, this new material serves a stable dielectric constant of 4.5 and dielectric loss less than 1% below 100 kHz, which do not change significantly over broad frequency range and temperature up to 150°C (melting point of ArPTU according to the DSC measurement is above 200 °C).

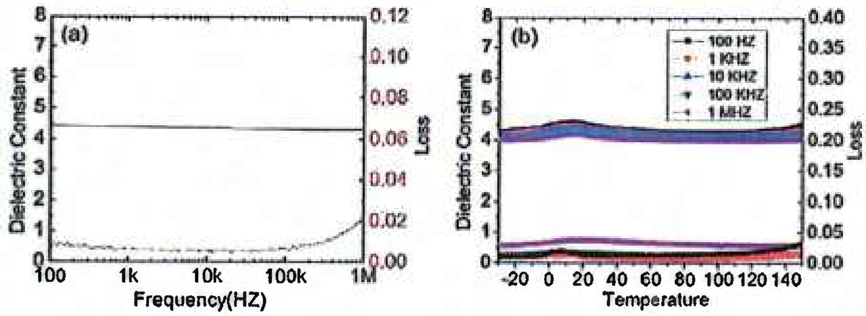


Figure 4. Dielectric constant and loss tangent from 100Hz to 1MHz at (a) room temperature; (b) temperature from 30°C to 150°C.

Figure 5(a) presents the charging-discharging curves (electric displacement D vs. applied electric field E) measured under different applied electric fields at 10 Hz. The ArPTU film exhibits a linear dielectric response to higher than 1 GV/m. The data also reveals that the dielectric loss, which is measured by the enclosed area between the charging and discharging curves, does not increase significantly at high fields. For comparison, the charge-discharging curves of BOPP films are also presented in figure 5(b). The discharged energy density and efficiency (= 1 – loss) of the ArPTU films and of the biaxially oriented polypropylene (BOPP) commercial films (3 μm thick) are presented in figure 6(a) and 6(b), respectively. At low fields (< 200 MV/m), the loss of BOPP is nearly zero due to very low dielectric loss (< 0.018%). The loss increases with field because of increased conduction, and above 500 MV/m, the dielectric loss of BOPP films becomes larger than that of ArPTU and continues to increase rapidly with field. [11, 16, 17] In contrast, the loss in ArPTU films slowly increases with field, while U_e is more than double of that of BOPP. Figure 6(a) shows that the discharged energy density of ArPTU reaches 24 J/cm^3 at 1.1 GV/m.

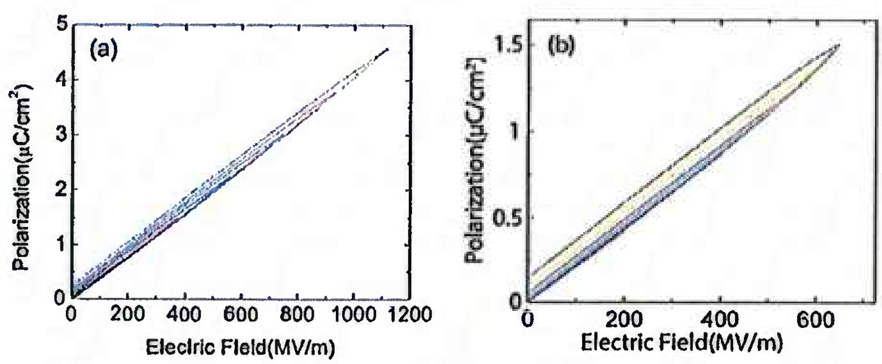


Figure 5. Polarization-electric field curves of (a) ArPTU under different electric field up to 1.1 GV/m at 10 Hz; (b) BOPP thin film

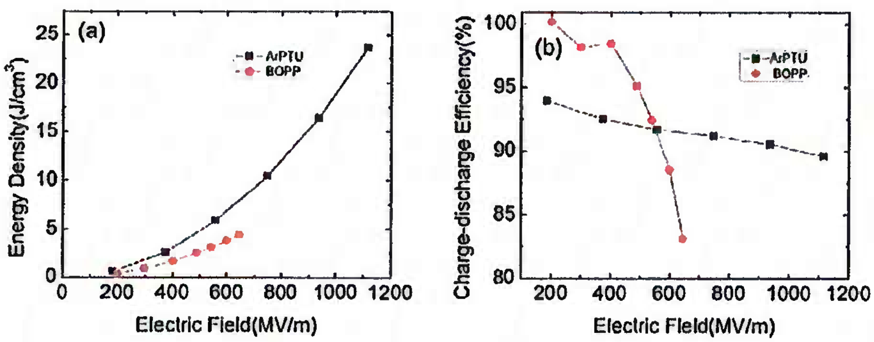


Figure 6. Comparison of ArPTU and BOPP (a) discharge energy density; (b) charge-discharge efficiency at high electric field.

The high field conduction was measured to characterize the conduction mechanism in this amorphous high polar glass phase materials (Figure 7). The conduction current in the ArPTU keeps a slow increase to the highest field of 1GV/m, where a relatively low value of 10^{-7} A/cm^2 was maintained. This is consistent with the high efficiency and low loss, especially the low conduction loss of the ArPTU in the charge-discharge curve. In the contract (figure 7 (b)), the BOPP thin films (3-4 μm) exhibit a conduction current of more than 2 orders of magnitudes higher than that of ArPTU.

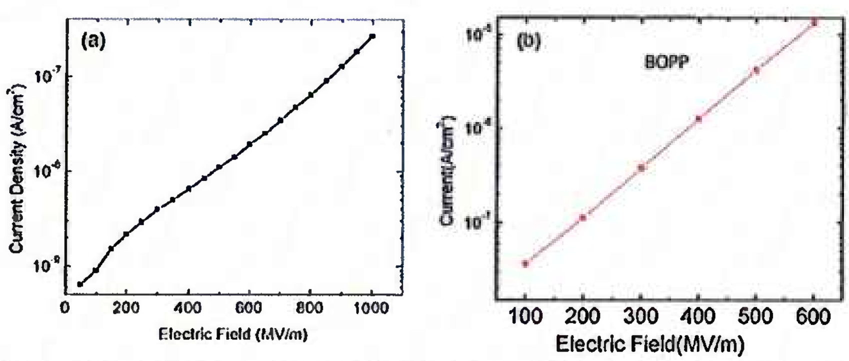


Figure 7. Room temperature current density vs. applied field for (a) ArPTU; (b) BOPP

High temperature charge discharge curves measurement of the ArPTU thin films was carried out and illustrated in figure 8. At temperature lower than 120°C, which is higher than the operation temperatures of many polymer dielectrics, a high efficiency (>90%) as well as a discharged energy density of 7 J/cm^3 at 600 MV/m can be maintained. However, the efficiency and discharged energy density start to drop when the temperature is higher than 120°C. The segmental motions of polymer chains at high temperature and high electric field may cause this thermal instability, and the high temperature glass phase to rubber phase transition will increase these segmental motions.

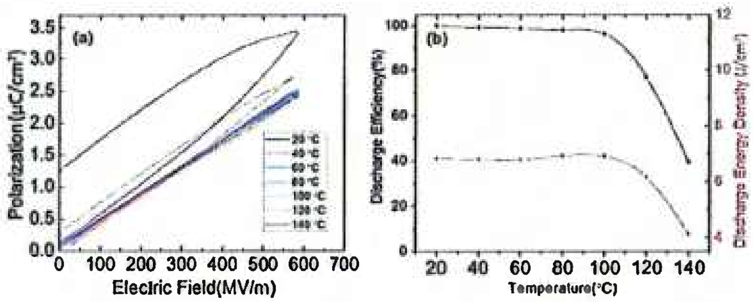


Figure 8. Temperature dependence of (a) charge-discharge curves of ArPTU; (b) discharge energy density and efficiency at 600 MV/m electric field

2.2. Relationship between the breakdown mechanism and surface morphology/thickness uniformity

Atomic Force Microscopy (AFM) images of the ArPTU films reveal a very smooth film surface in small areas on each sample (Figure 9). For a 5 μm thick film with a breakdown field ~ 1 GV/m, the surface roughness is less than 0.16 nm (rms value) over a 5 μm square area.

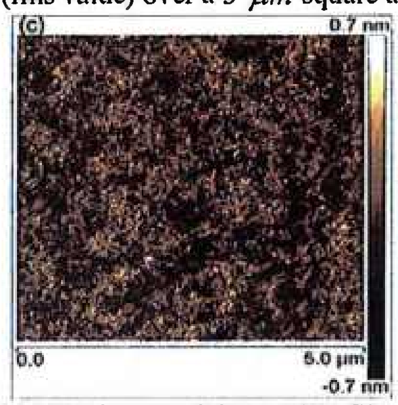


Figure 9. AFM image of the ArPTU film (5 μm thick)

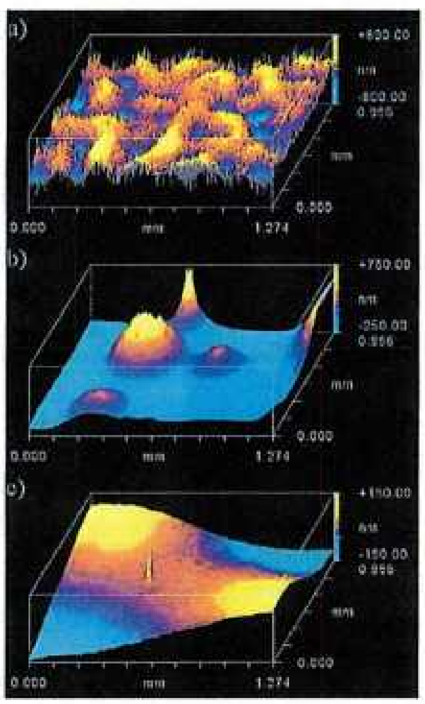


Figure 10. Optical profilometry image of ArPTU thin films (1 μm to 2 μm thickness)

In the thin film fabrication process, the environment conditions are of great importance. The different drying speed of the solvent caused by the temperature, pressure will lead to different surface morphologies and different surface defects level, which is one reason of the Weibull distribution. To study the large area morphology, the optical profilometry was carried to get the information of the film surface on 1.2mm^2 area. In figure 10 (a) and (b), the low quality samples show a very rough surface with thickness variation and pinholes all over the whole samples, which have a 144 nm and 78nm RMS surface roughness, respectively. This feature is such a crucial issue for the high electric field performance, cause the pinholes and surface defects will induce the local electric field difference, increase the electric conduction in those areas, and then lead to failure of the whole sample. Different from the sample (a) and (b), the sample in 10 (c) illustrates an extremely flat surface with 7nm RMS surface roughness as well as a uniform thickness of 1 um. This remarkable value is quite unique especially in the organic materials, and leads to a higher average breakdown voltage in Figure 11.

This relationship between the surface morphology and high field performance such as the dielectric strength was proved in the Weibull distributions (figure 11) below; where the samples with the higher surface defects have obviously low breakdown strength below 500 MV/m. The smoothest samples (0.16nm on 5μm by 5μm area; 7nm rms on 1.2 mm^2 area) serve the highest performance of an average around 600~700 MV/m electric strength and a highest breakdown more than 1.1 GV/m.

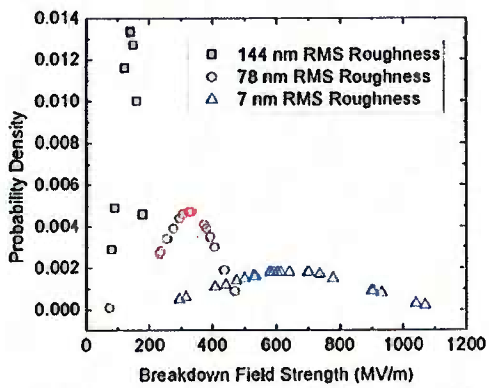


Figure 11. Breakdown field strengths of ArPTU with different surface roughness values

2.3. Discussions

To get more understanding of the possible causes of the observed low dielectric loss and high breakdown field in the ArPTU films, an x-ray diffraction measurement was carried out. The data, presented in figure 12 (a), shows that the ArPTU films are virtually amorphous with a broad dielectric peak around 2 theta=19°. This corresponds to a polymer structure as illustrated in figure 12(b). It was also found that annealing of the films at 200 °C does not change the amorphous structure. This is quite different from BOPP which is a semicrystalline polymer and has a glass transition temperature below room temperature (T_g < 240 K).[13] Above T_g, the segmental motions of polymer chains will facilitate charge hopping, which increases exponentially with the applied electric field, and leads to the observed increase in conduction loss at high electric field. [16-18] This suggests that the presence of random dipoles and the amorphous, glass-phase structure in ArPTU provides substantially stronger scattering to charge carriers and results in much smaller conduction compared with the non-polar polymers. [16,17] The coulombic interaction between dipoles and charge carriers causes extra scattering in addition to the phonon-electron scattering,[18] which reduces the conduction current and improve dielectric strength by stabilizing the electron energy.[19] Moreover, when the dipole moment exceeds a

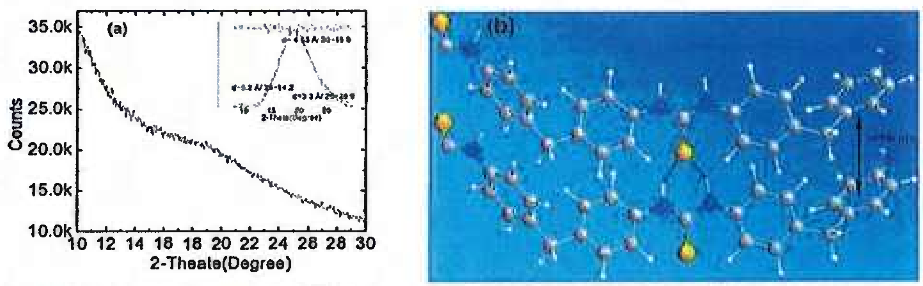


Figure 12. (a)Wide-angle x-ray diffraction of the ArPTU films; (b) Molecular structure diagram of the ArPTU.

certain critical value, the polar groups can also act as traps.[21,22] For instance, for the coulomb field generated by a dipole with dipole moment D, quantum mechanical analysis shows that bounded states will exist if the following condition is satisfied:[21]

$$\frac{D}{q\varepsilon a_o} > 0.64 \tag{1}$$

Here $q = 1.6\times10^{-19}$ C is the elementary charge, $a_0 = 5.29\times10^{-11}$ m is the Bohr radius, and ε is the effective dielectric constant that represents the dielectric screening effect due to the medium. Considering the ultra-short electron transit time between scattering events under very high electric field, the optical frequency dielectric constant $\varepsilon \sim 2.6$ is used for estimation (corresponding to the refractive indexes of about 1.6 for polythiourea),[24] which leads to a critical dipole moment of about 4.2 D. This suggests that the highly polar thiourea groups (dipole moment ~ 4.89 D) in ArPTU would very likely act as traps for the electrons. The traps reduce the amount of conduction carriers and results in an apparent carrier mobility μ expressed by,

$$\mu = \mu_0[\frac{N_t}{N_{eff}}\exp(\frac{\Delta E_t}{k_B T})]^{-1} \tag{2}$$

where μ_0 is the trap-free mobility, N_t is the trap density, N_{eff} is the effective density of states for the conduction band, ΔE_t is the trap depth, k_B is Boltzmann's constant, and T is the temperature.[20] This apparent mobility can be many orders of magnitude lower than the intrinsic carrier mobility, which explains the strong suppression of the conduction current.[17] This mechanism is also supported by experimental observations by Ishino et al, which show that polyethylene copolymers with highly polar groups exhibited higher breakdown strength and lower high-field conduction loss than pure polyethylene.[24] Also in that work, polar copolymer charge traps with depths of about 0.4 eV were detected.[24] In these ethylene copolymers, the concentration of polar groups was limited to <1 mol% due to possible defects generated at higher concentration, whereas in the ArPTU the highly polar thiourea groups appear in each monomer unit and result in stronger suppression of the charge conduction. Finally, having a uniform film is also very important to the electric characteristics of the materials, and Atomic Force Microscopy (AFM) images of the ArPTU films reveal a very smooth film surface. For a 5 μm thick film with a breakdown field ~ 1 GV/m, the surface roughness is less than 0.16 nm (rms value) over a 5 μm square area (see figure 10). This implies low surface defect levels, which are known to lower the breakdown field and increase the conduction loss due to trap assisted hopping of charge carriers.[18]

The results of this study demonstrate the promise of aromatic, amorphous, polar polymers containing high dipolar moments with very low defect levels for future dielectric materials with ultra-high electric energy density, low loss at high application fields, and ultra-high breakdown fields. Specifically, we showed that aromatic polythiourea films exhibit an ultrahigh breakdown field (> 1 GV/m) and maintain low loss characteristics up to the highest field measured. As a result, the ArPTU films display an energy density higher than 24 J/cm^3. These dielectric responses are superior to the high field dielectric behavior of the state-of-the-art low loss BOPP as well as the modified PVDF ferroelectric polymers.

3. Study of conduction mechanisms and defects structures that are responsible for the high energy density and low loss in the aromatic polythiourea dielectric films

3.1. High field conduction of aromatic polythiourea thin films

The exponential nature of the current voltage relationship shown in Figure 13 is indicative of hopping conduction, where localized carriers jump between resonant energy states in the direction of the electric field. [18, 25-28] Hopping conduction is typical in disordered organic materials and features substantially lower carrier mobilities than that in the band conducting crystalline materials, hence improves the conduction loss. In amorphous materials, electron and ionic hopping can be modeled by the equation:

$$J = 2qn\lambda v * \exp(-U/kT) * \sinh(\lambda qE/2kT) \qquad (3)$$

where q is the charge of the carriers, n is the carrier concentration, λ is the ionic/ electronic hop distance, v is the escape frequency, U is the barrier height of trap sites, k is Boltzmann's constant, T is the temperature, and E is the electric field. [18, 29] In the conduction measurement, there is a high transient charging current when the voltage is applied. After several seconds, a steady state current emerges in ArPTU, which is due primarily to electronic conduction. Since ions cannot be injected from the contacts, ionic conduction may be a portion of the transient current, but is not significant at steady state. In our measurement, a 20 second current stabilization delay was introduced at each voltage step to ensure that only the electronic contribution is being measured.

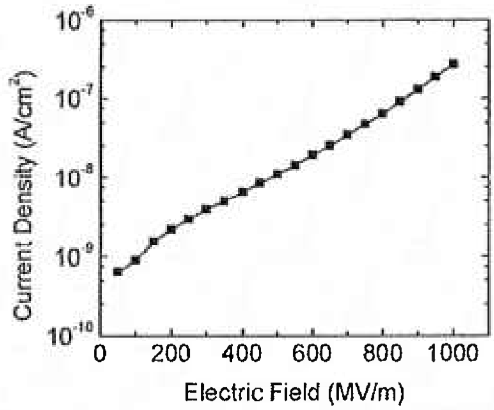


Figure 13. Current density vs. applied field of ArPTU

In general, the conduction current depends on the trapping levels, temperature, hopping distance, and escape frequency, which can be simplified into a quasi-steady-state current density equation with lumped parameters: $J = J_0 \sinh(\alpha E)$ (4)
where J_0 and α are constants related to trap concentration, hopping distance, and the barrier height of trap sites; and E is the electric field in MV/m. [18, 29] The fitting of equation 4 to the data in Figure 13 leads to $J_0 = 6 \cdot 10^{-10}$ A/cm^2 and $\alpha = 6$ cm/V. J_0, which depends on trap depth, temperature, and carrier density can be regarded as the current at low electric field (E approaches zero). The $J_0 = 6 \cdot 10^{-10}$ A/cm^2 value in ArPTU is high, compared to low-loss insulating polymers such as polypropylene. For example, J_0 in semicrystalline polypropylene is typically between $2 \cdot 10^{-14}$ A/cm^2 and $3 \cdot 10^{-13}$ A/cm^2 depending on the crystallinity.[29] This extremely low low-field current explains why there is virtually no conduction loss in polypropylene at low voltages,[22] and the higher starting current in ArPTU explains the higher measured loss (>5% at 100 MV/m).

The second parameter, α, is related to hop distance and temperature, and determines how fast the current density increases with electric field. The value measured in ArPTU (6 cm/V) is almost three times lower than a typical value in polypropylene (>16.6 cm/V),[29] which is consistent with the low loss behavior at high fields for the ArPTU. At high-fields, the current density in ArPTU remains low (~0.2 ▯A/cm^2 at 1 GV/m) which results in a low loss (10% at 1 GV/m), compared with BOPP. [14]

3.2. Characterization of traps in the ArPTU

The presence of random dipoles with high dipole moment in ArPTU provides substantially stronger scattering to the charge carriers and results in much smaller conduction compared with the non-polar polymers. The coulombic interaction between dipoles and charge carriers causes extra scattering in addition to the phonon-electron scattering,[29] which reduces the conduction current and improve dielectric strength by stabilizing the electron energy.[14] Moreover, when the dipole moment exceeds a certain critical value, the polar groups can also act as traps. [14, 30] For instance, for the coulomb field generated by a dipole with dipole moment D, quantum mechanical analysis shows that bounded states will exist if the following condition is satisfied:[30]

$$\frac{D}{q\varepsilon a_0} > 0.64 \tag{5}$$

Here $q=1.6\times10^{-19}$ C is the elementary charge, $a=5.2\times10^{-11}$ m is the Bohr radius, and ε is the effective dielectric constant that represents the dielectric screening effect due to the medium. Considering the ultra-short electron transit time between scattering events under very high electric field, the optical frequency dielectric constant $\varepsilon\approx2.6$ is used for estimation (corresponding to the refractive indexes of about 1.6 for polythiourea),[31] which leads to a critical dipole moment of about 4.2 D. This suggests that the highly polar thiourea groups (dipole moment ~ 4.89 D) in ArPTU would very likely act as deep traps for the electrons. The traps reduce the amount of conduction carriers and results in an apparent carrier mobility □,

$$\mu = \mu_0\left(\frac{N_t}{N_{eff}}\exp\left(\frac{\Delta E_t}{k_B T}\right)\right)^{-1} \tag{6}$$

where □$_0$ is the trap-free mobility, N_t is the trap density, N_{eff} is the effective density of states for the conduction band, ΔE_t is the trap depth, k_B is Boltzmann's constant, and T is the temperature.

Charge storage and charge transportation in the organic/inorganic materials are an important subject for many applications, whereas the dielectric polymers usually have complicated structures and very low conductivity, which make it difficult to characterize. To study the charge storage, decay, and transportation in the ArPTU, a systematic thermally stimulated discharge current (TSDC) measurement was carried out. [31-35] In the TSDC, the electric charges are injected to the dielectrics by optical or electrical techniques and by measuring the charge decay and the discharge current at constant heating rate, the energy levels, charge storage properties, surface voltage stability, relaxation time, activation energy of trap, etc., in the dielectrics can be investigated.

Based on the dielectric theory [36], the depolarization current in the TSDC can be expressed as,

$$I(T) = (Np^2\alpha E_p/kT_p\tau_0)\exp\left[-\frac{U}{kT}-(1/b\tau_0)\int_{T_0}^{T}\exp\left(-\frac{U}{kT}\right)dT\right] \tag{7}$$

where N is the number of dipoles per unit volume, p is the dipole moment, E_p is the polarizing field, T_p is the polarizing temperature, α is a geometrical factor, τ_0, b are constant, k is the Boltzmann constant, U is the activation energy (potential barrier between the normal state and activated state).

The low temperature tail of the TSDC can be deduced from Eq. (7) as,

$$lnI(T) = const - U/kT \tag{8}$$

And hence the activation energy U can be determined from a semi logarithmic plot of I(T) vs. 1/T(initial rise method)

In this study, 4-micron ArPTU films were used for the TSDC characterization. Gold electrodes of 6 mm diameter were sputtered onto the film surfaces. For the TSDC characterization, the films were first poled at 10 KV/mm field and 120°C poling temperature for 10 minutes. Then the films were cooled down to -130°C under the poling electric field. At --130 °C, the poling field was removed. The current density vs. temperature at a constant heating rate of 5 degree/per minutes was characterized using a Cascade Microtech Probe State with an HP 4140B pA meter/DC voltage source and a Model BOP 1000M Kepko Bipolar Operational Power Supply/Amplifier.

Figure 14 presented a typical thermally stimulated current vs. temperature for the ArPTU films. There are two peaks observed in the thermal stimulated discharge current, which are at 176 K and 397 K (table 1), with the peak currents of 8 *pA* and 50 *pA*, respectively. From the data, the trap levels of 0.25 eV and 2 eV, high electron trap density of $10^{14}/cm^3$ and $10^{15}/cm^3$, were deduced. Compared with the polypropylene, the state-of-the-art dielectric polymer which is a non-polar polymer and has a low energy trap (<1 eV), ArPTU with high dipole moment and dipole density has deeper traps (>2 eV) and higher trap density ($>10^{15}/cm^3$).

Table 1 Summary of results of ArPTU films

	Peak temperature T_m(K)	**Peak current $I(T_m)(10^{-12})$**	**U(eV) (Initial rise method)**	**Electrons trapped density**
Low temp. peak	176	8	0.25	$\sim 10^{14}/cm^3$
High temp. Peak	397	50	2	$\sim 10^{15}/cm^3$

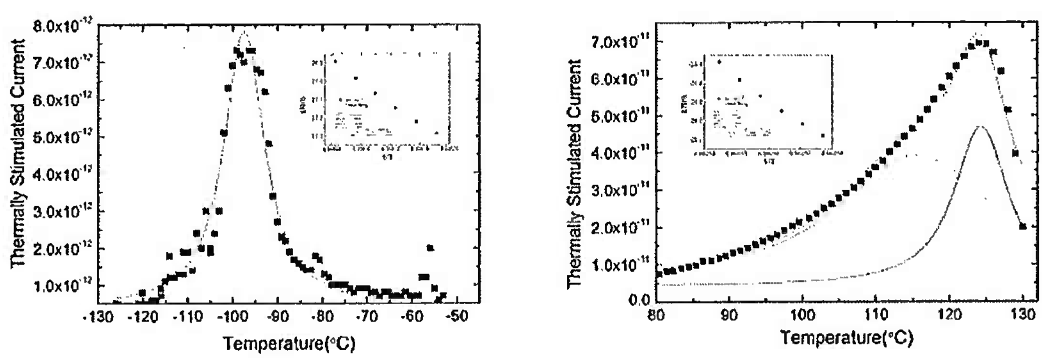


Figure 14. Thermally stimulated current vs. temperature of ArPTU films

4. Aromatic polyureas with tailored molecular nano-structures and dielectric response

Developing polymers with high dielectric constant and low loss is attractive for the modern electric devices and electronics, while the high energy density, low loss, and high operation temperature are required for the energy storage applications. Besides the aromatic polythiourea, aromatic polyurea P(MDA/MDI) as a polymer dielectric for high temperature and high energy density capacitor application has been investigated by Wang et al. earlier.[37] The flexible molecular structures of both polyureas and polythioureas provide attractive dielectric systems to tailor systematically the molecular structures and study the dielectric responses.

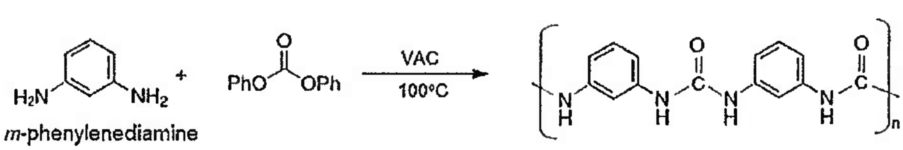
In the strongly dipolar polymer materials such as the polyurea and polythiourea with dipole moment larger than 4 Debye, the dipolar orientation polarization is dominant polarization process compared with the electronic, atomic, and ionic polarizations. The Frohlich model, which has been used widely to describe the dipolar polarization in the dielectrics, takes both the short-range interaction between molecules and the deformation polarizations into account compared with other models.[18] In Frohlich model, the dielectric constant, or the relative permittivity, is proportional to the square of dipole moment, volumetric dipole density, and correlation factor between the dipoles. Frohlich equation:

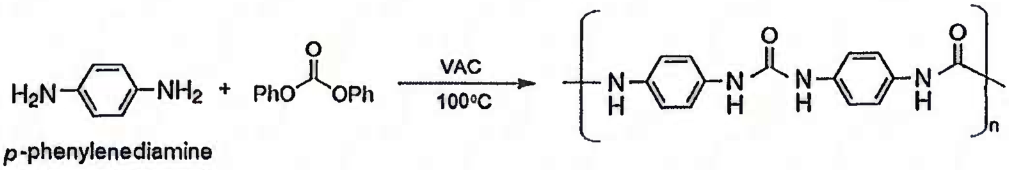
$$\frac{(\varepsilon_{rs} - \varepsilon_{r\infty})(2\varepsilon_{rs} + \varepsilon_{r\infty})}{\varepsilon_{rs}(\varepsilon_{r\infty} + 2)^2} = \frac{Ngu^2}{9\varepsilon_0 kT} \tag{9}$$

$$\varepsilon_r \propto Ngp^2 \tag{10}$$

where ε_{rs}, $\varepsilon_{r\infty}$ are the dielectric constant at low frequency and optical frequency, respectively, N is the volumetric dipole density, g is the correlation factor, u is the dipole moment, k is the Boltzmann constant, and T is the temperature. With a high dipole moment of 4.56 Debye in the urea unit, the dielectric constant will be enhanced if a high volumetric dipole density can be achieved. In the aromatic polyurea P(MDA/MDI) with dielectric constant of 4.2, the two aromatic ring, which acts as the blocking structure, leads to a relatively low volumetric dipole density because of the large size of the molecule. Here, a new aromatic polyurea with a higher volumetric dipole density by replacing the two aromatic rings with one was proposed, synthesized, and studied.

Traditionally the aromatic polyureas were synthesized via polycondensation of aromatic diamine and aromatic diisocyanate. Besides, chemical vapor deposition has also used to synethsize small scale aromatic polyurea films.[37] In this study, a green synthetic process for a new type of polyurea (Scheme 2) was developed which provides a new route for synthesis of various new polyureas with the advantages of isocyanate free, solvent free, catalyst free, easy to remove by-product.





Scheme 2. Synthesis of polyurea

The blocking structures between the urea dipoles in the polymer chains can be modified, thus, it is possible to synthesize new types of polyureas with tunable dielectric properties. Both meta and para aromatic polyureas were synthesized in this study. However, because of the low solubility and low quality film of the current para-PU, only the meta-PU films are studied and results are presented here. The dielectric constant of the one-ring aromatic (meta) polyurea is 5.6, higher than the traditional polyureas. The films show a relatively high temperature stability (up to 160°C as shown in figure 15). Figure 16 presents the high field dielectric response of the meta-PU, with a high electric breakdown field of 660 MV/m, as well as a high polarization. A discharged energy density of > 13 J/cm^3, and charge-discharge efficiency ~ 91% were obtained at 670 MV/m electric field. Compared to the P(MDA/MDI) which has two aromatic rings and has a discharged energy density of 8 J/cm^3 at 660 MV/m, the meta-PU exhibits a higher energy density at the same electric field because of the high dielectric constant. In the next step, the detailed dielectric breakdown of meta-polyurea will be studied and improved to achieve higher energy density and lower losses.

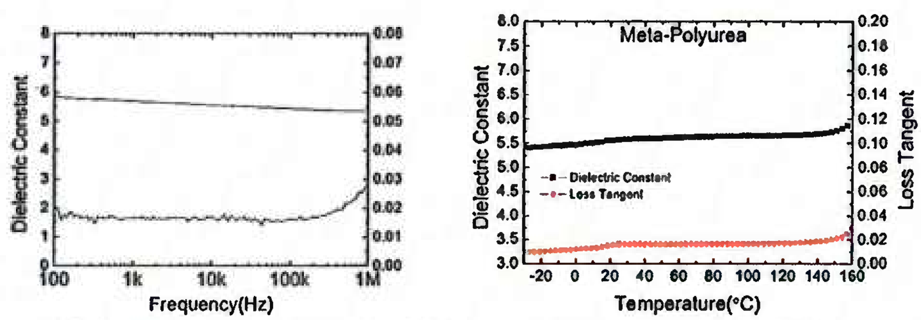


Figure 15. Dielectric properties of m-PU at room temperature (left); different temperature (right)

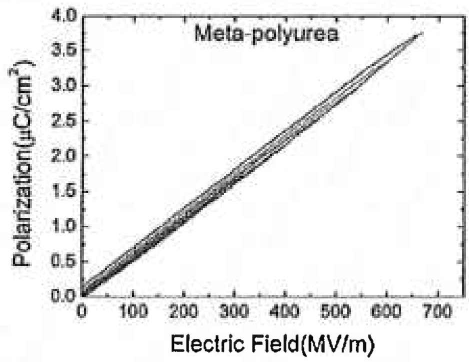


Figure 16. Polarization-electric field curves of meta-polyurea at 10 Hz.

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